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RESULTS OF MEASUREMENTS OF SPIN LATTICE RELAXATION TIMES IN LIQUIDS
OBTAINED IN THE CRACOW LABORATORY OF NUCLEAR MAGNETIC RESONANCE

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The preliminary results of the investigation of spin-lattice rela-
xation times in liquids obtained in the Cracow Laboratory of the Nuclear
Magnetic Resonance are described. We used the metod of measurements
presented in the previous communication by Hennel and Hrynkiewicz.

Spin-lattice relaxation time in very pure water

The Bloembergen, Purcell and Pound theory of the spin-lattice
relaxation times /1/ gave for pure water at $20^{o}C$ T_1 = $3\cdot4$ sec.
When to their calculation the correction made by Kubo and Tomita /2/
is introduced and when the newest values of atomic constants are used
the theoretical value of T_1 for water amounts $2\cdot5$ sec. As it is well
known this value must be regarded as an approximate one because of the
simplifications of the model on which base the theory of relaxation
times is developed.

The experimental values published by Giulotto and collaborators
for water at $20^{o}C$ carefuly purified from oxygen are /$3\cdot6\pm0\cdot2$/ sec /3/
/$3\cdot5\pm0\cdot35$/ sec /4/ and $3\cdot1$ sec /5/.

In our measurements we used several samples of water sealed in
glass and quartz tubes. The water was very carefuly purified by a
chemical method, made oxygen free by long boiling and sealed in vacuum.
Our result at $20^{o}C$ is /$3\cdot21\pm0\cdot07$/sec.
On the last Colloque AMPERE Giulotto presented the temperature dependence
of the water relaxation time T_1 He obtained a slow decrease of the
expression η T_1/T with increasing temperature, while the BPP theory
predicts the constant value of this expression. We obtained the similar
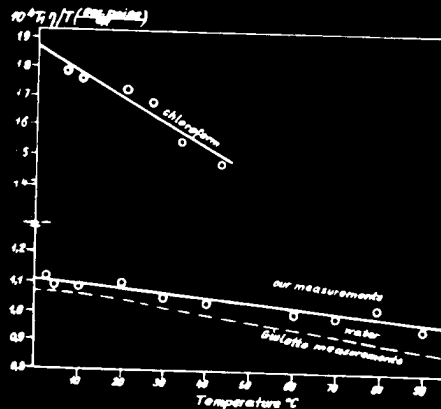dependence as found by Giulotto. The results are represented on Fig.1.

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Fig.1. Temperature dependence of η T_1/T for water and chloroform.

We tried to ontroduce to the theoretical value of T_1 the correction proposed by Seiden /6/ based on the distribution of water molecules at different temperatures measured by Morgan and Warren /7/ by means of X-ray diffracticn. We obtained that while this correction changes the absolute value of T_1, it cannot explain the temperature dependence of η T_1/T given by the experiment.

Spin-lattice relaxation time in pure chloroform.

The chloroform molecule contains only one proton so the main role in the spin-lattice relaxation plays the itermolecular interaction. The intramolecular interection between proton and chlorine nuclei, astimated on the base of BPP theory is small one. In this case can be expected the much longer T_1 than for two or more proton molecules. Our measurements gave for pure chlorcform free of oxygen at $20^{\circ}C$ T_1 = /90 ± 4 $\boldsymbol{j\eta\eta}$/ sec. The temperature dependence of η T_1/T shown also on Fig.1 is much higher than for water. Between temperatures $5^{\circ}C$ and $40^{\circ}C$ η T_1/T decreases by câ 18 per cent. Thedecrease for water over the same range of temperatures amounts only câ 6 per cent. The measurements of the temperature dependence of T_1 for other liquids are in preparation to answer the question if the observed decrease of η T_1/T is connected with only the translational part of the spin-lattice relaxation time.

Spin-lattice relaxation times in water solutions of gelatin.

On Fig. 2 is shown the temperature dependence of spin-lattice relaxation times for different concentrations of gelatin solutions in water.
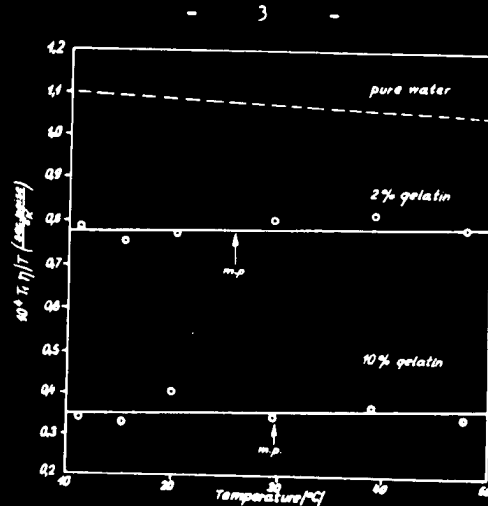
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Fig.2.   Temperature dependence of T_1 for water solutions of gelatin.

        For calculation of η T_1/T expressions the viscosity of a pure
water was taken. It is clearly seen from the diagrams, that η T_1/T
calculated in this manner is nearly constant over a rather wide range
of temperatures. It means that though the macroviscosity of the gelatin
solution changes much more than that of water, the relaxation in water
is governed by its own viscosity. It is worthwhile to notice that at
the melting point of gelatin, where is a big jump of the macroviscosity,
no jump of T_1 can be observed. The shift of curves to lower values for
more concentrated solutions is caused by paramagnetic impurities contained
in gelatin. Our results prove that for investgated concentrations the
main part of water molecules can be regarded as free filling the cavities
between gelatin molecules.

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METHOD OF MEASUREMENT OF LONG SPIN-LATTICE RELAXATION TIMES IN LIQUIDS

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Introduction

In the few last years the question of nuclear spin-lattice relaxation
time T_1 of liquids became important in spite of its significance as a
means for investigation of the structure of liquids. In this situation
the problem of the method of precision measurements of T_1 is very actual.

Till now the methods most frequently used 1 are:
/1/ the direct method, /2/ the progressive saturation method, /3/ the
method worked out by L. Giulotto and coll.[2] based on the Bloch's adiabatic
rapid passage.

The direct method relies on observation of the growth of the nuclear
resonance line that has been saturated before. During the observation the
high frequency magnetic field H_1 should be small enough to additional
saturation. The accuracy of this method is rather a low one. Bloembergen[3]
Purcell and Pound estimate the error of their measurement of T_1 in water
at $20^{\circ}C$ for 20 per cent.

The progressive saturation method gives only the posibility of the
measurement of the ratio of spin-lattice relaxation times T_1 for two
samples. So it can be used only in connection with another absolute method.
The progressive saturation method is especially convenient for measurements
of short relaxation times.

The most exact method known till now is the Giulotto method [2].
It depends on measurement of the height of resonance lines for different
time intervals between the adiabatic passages through the resonance
conditions. If a correct value of the spin lattice relaxation time is to
be obtained the following conditions must be fulfiled

$$H_1 \gg \omega_m H_m \qquad /1/ \qquad H_1 \ll \mathcal{T} H_m \qquad /3/$$

$$\frac{\pi}{\omega_m} \text{ of the order of } T_1 \qquad /2/$$

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Where γ - gyromagnetic ratio of the nunleus

H_1 - r.f. magnetic field amplitude

H_m - modulating magnetic field amplitude

ω_m - circular frequency of the modulating magnetic field

T_1 - spin-lattice nuclear relaxation time

The difficulty in this method comes from the fact that the simultaneous fulfilment, of conditions mentioned above often causes great difficulties of practical nature. E.g. if T_1 = 2,35 sec, $\frac{\pi}{\omega_m} \approx T_1$ and is demanded all inequalities to be fulfiled with a factor of 100 the r.f. field should be H_1=1 gauss and the modulation field H_m=200 gauss. Practically it is very difficult to obtain such a high modulation field in a gap of an electromagnet.

D e s c r i p t i o n   o f   t h e   m e t h o d.

To overcome the difficulties mentioned above a following method was worked out. The measurement of spin-lattice relaxation time of liquid sample consists of two separate parts: the measurement of the completely desaturated nuclear magnetization M and the measurement of the momentary values of the vector M during the time of his growth from zero after a complete saturation.

The nuclear magnetic resonance device is arranged in such a way that it is possible to change alternatively the frequency of the current in the modulating coils. This can be done by means of a single switch. The used magnetic field modulations are ω'_m = 2π 50 sec^{-1}

H'_m=2 gauss and ω_m=2π . 0,3 sec^{-1} H_m=6 gauss. This last type of modulation is made by means of an electrolytic potentiometer [2] moved by an electric motor. When the motor is not running it is possible to set the rotating electrode of the potentiometer in the desired position.

The output of the nuclear resonance detecting apparatus is recorded on a photographic paper tape by means of a mirror oscillograph.

The course of the magnetic field modulation is shown on fig.1. The central value of the magnetic field is exactly the resonance one H_o. At first the rotating electrode of the electrolytic modulator is set in one of its extreme position. /e.g. the lower one/ and the higher frequency modulation current is switched on. If the proper value of the radio frequency magnetic field H_1 is used the sample is completely saturated after a few seconds. The authors used H_1=0.25 gauss for the relaxation time range over 0.7 - 100 sec. When the lines do not disappear completely

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in spite of the phase memory about 5% /in amplitude/ of about 30 c.p.s.
modulation was added to the 50 c.p.s. modulation for destruction of this
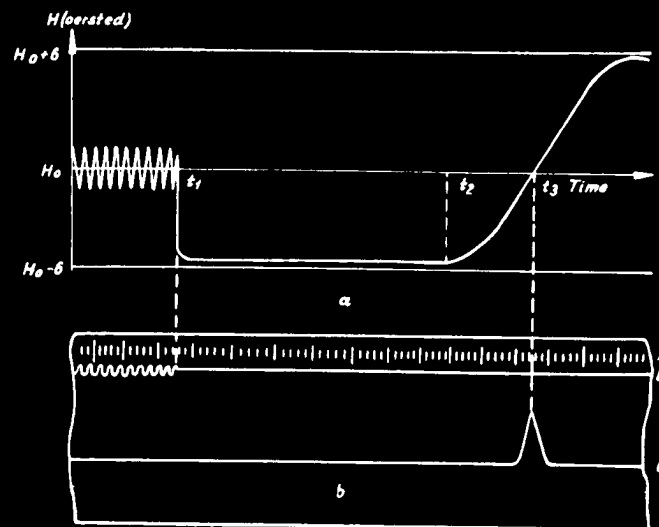memory.

Fig. 1 Method of T_1 measurement, a - magnetic field vs. time,
b - record of the mirror oscillograph.

After the sample is completely saturated by means of the 50 c.p.s.
modulation the switch is turned to the second position and the modulation
coils are conected with the electrolytic potentiometer. In this moment
/ t_1 on figure 1/ the magnetic field intensity jumps to the lower extreme
value because of the initial position of the rotating electrode. Since
this time the sample is very far away from the resonance conditions and
the growth of the nuclear magnetization goes without external perturbation.
The next passage through the resonance value /moment t_3/ can be made by
setting in motion the electrolytic modulator in a suitable chosen moment t_2.

If the time interval t_3-t_1 /i.e. the free growth time/ is suffitiently
long $t_3-t_1 > 5T_1$ the height of the recorded line is proportional to the
completely desaturated value of the nuclear magnetization M_∞ . The momentary
values of magnetization vector M during its growth can be obtained by
chosing a shorten time interval $t_3 - t_1$. We evaluated that the best accuracy
can be obtained if $0,6 \ T_1 < t_3 - t_1 < 1,5T_1$. The most practical way is
to make one M_∞ record, immediately three or four M records and then one

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M_∞ record again. The equality of both M_∞ indicates that the amplification
factor did not change during the whole measurement.

The measurement of the $t_3 - t_1$ time can be done by means of the stop
clock if this is a long one. In the case of short time intervals the
measurement can be done using the time marks /A on fig.1/. Then the mirror
oscillograph must have three separate mirror devices: for the output
record /C/, for the time marks /A/ and for the t_1 moment record /B/. This
last mirror device is connected with the 50 c.p.s. modulation circuit.

The evaluation of T_1 from the data obtained in this manner is done
by means of a plot - ln /1-M/M_∞ / versus $t_3 - t_1$ /fig. 2/.

It is also very useful to make a control diagram of exp/-t/T_1/ versus
M putting for T_1 the obtained value /fig.3/. If the measurement is correct
all points should lie on a straight line /of course if the sample obeyed
the single exponential increase law/ which intersects the vertical axis
in point 1 and the horizontal axis in point M_∞ . Even a small error in
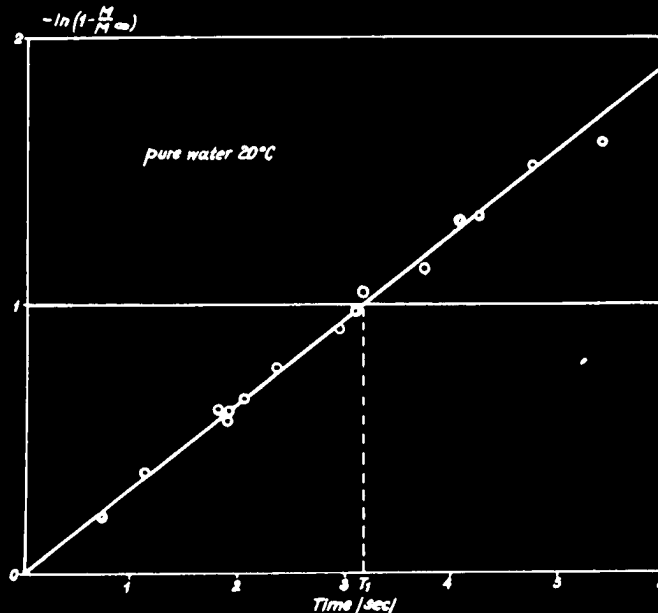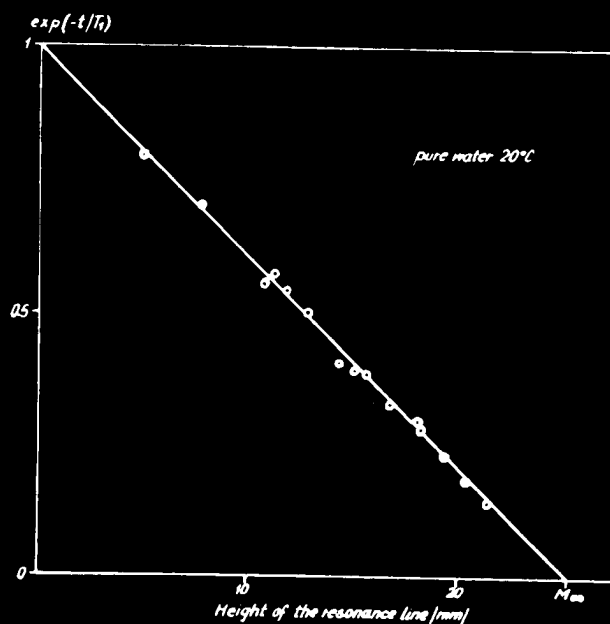M_∞ can be found this way.

Fig. 2 Growth of the magnetization M in time

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Fig. 3. Control diagram for M_∞

Discussion

Using the described method it is possible to observe the nuclear relaxation process phenomenon with lower than in other methods pertutbations introduced by the nuclear resonance apparatus. This comes from the fact that using the other methods it is necessary to fulfil several conditions /mentioned above/ which practically are difficult or even not possible to satisfy simultaneously.

Using the described method it is necessary to fulfil only tree conditions which do not cause technical difficulties. These conditions are:

The time of passage $\mathcal{T} \ll T_1$ where $\mathcal{T} \approx \dfrac{H_1}{\omega_m H_m}$ /4/

H_m = const. /5/

ω_m = const. /6/

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The described method in comparison with Giulotto's does not require the fulfilment of the adiabatic passage condition /1/ and the condition /2/ which connects T_1 with ω_m.

Our method was succesfully used in Cracow Laboratory for measurements of spin-lattice relaxation times in liquids over the range 0,5 - 100 sec. The accurancy of measurement of T_1 for pure water in 20°C is estimated as less than 3 per cent.

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